

PATENT SPECIFICATION

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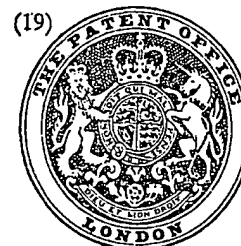
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(54) GRAPHITE PELLETS

(71) We, THE BRITISH PETROLEUM COMPANY LIMITED, of Britannic House, Moor Lane, London, E.C.2, a company incorporated in accordance with the Laws of England, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention relates to pellets of a carbon product having a large surface and the use of the pellets in the separation of hydrocarbons.

Finely ground graphites prepared by grinding in vacuum or in a gas e.g. air are well known, and in this specification are termed vacuum ground or "gas-ground graphites". It is also known that finely ground graphites have selective absorption properties e.g. British Patent No. 1,126,482 discloses a method of separating long-chain normal hydrocarbons having at least 10 carbon atoms per molecule from their mixtures with other hydrocarbons by contacting the mixture with graphite having a surface area of at least 50m²/gm, to absorb selectively the normal hydrocarbons.

However gas or vacuum graphites suffer from the disadvantage that finely ground graphite can only be used in the form of a slurry.

It has now been found that the graphite can be formed into pellets by compounding with a binder. The pellets can be used in the form of a fixed bed and have the further advantage in that a counter-current process can be used.

Thus according to the present invention there are provided graphite-containing pellets comprising graphite with a binder comprising finely divided alumina said graphite being a vacuum or gas ground graphite having a surface area of 50 to 2000 m²/gm (BET).

By the term "finely-divided alumina" we mean alumina having a surface area in the range 1 to 1000 m²/gm.

The term "alumina" is intended to embrace both hydrated alumina and anhydrous alumina.

[Price 25p]

Preferably the alumina has a surface area in the range 100 to 600 m²/gm.

The finely divided alumina is preferably (i) a colloidal alumina manufactured by Du Pont and sold under the name "Baymal" (Registered Trade Mark) and having a surface area of 350 m²/gm, this material is a micro-crystalline fibrous boehmite and is α -alumina monohydrate or (ii) a colloidal alumina manufactured by Laporte and described as "Dispersible alumina" and designated RD 12026. The preparation of the "Baymal" alumina is described in USP 2,915,475.

The US Patent 2,915,475 discloses the preparation of fibrous Boehmite (α -alumina monohydrate) and describes the alumina as being in the form of small fibrils (the word "fibril" meaning an individual crystalline particle) in the shape of laths, at least two of the dimensions of which are in the colloidal range. The laths have their two smaller dimensions in the range 3 to 15 nanometers whilst their axial ratio, their ratio between their length and smaller dimensions, falls in the range 50:1 to 150:1. "Baymal" (Registered Trade Mark) which has a surface area of about 350 m²/gm would have fibrils having their small dimensions at about 4 nanometers and lengths of between 200 and 600 nanometers. Depending on the conditions of manufacture the fibrils may agglomerate to give thread like aggregates called fibres which may show only partial colloidal properties.

The pellets may contain from 5 to 50% by weight of alumina binder preferably 15 to 40%.

According to another aspect of the present invention there is provided a process for the preparation of graphite-containing pellets which process comprises intimately mixing a vacuum or gas-ground graphite powder having a surface area of 50 to 2000 m²/gm with a finely divided alumina binder, working the mixture into a paste with a suitable liquid and granulating or extruding through a die.

The graphite and the alumina can be mixed either wet or dry. In dry mixing satisfactory

results have been obtained by ball milling but high speed mixing in e.g. a Universal High Speed mixer Type TLEHK—8 made by Gunter Papenmeier A.G. is preferred. In wet mixing it is preferred to mix using a High Speed Mixer or a colloid mill e.g. a colloid mill made by Premier Colloid Mills Ltd. using a gap of 1.016×10^{-4} m between the stones. The granulation can be effected by spreading the paste out on a tray, allowing to dry and breaking up the cake so formed.

After extrusion or granulation the extrudate or granules are preferably dried, broken up and sintered in nitrogen for 24 hours at 400°C.

The extruded pellets thus prepared are mechanically strong and stable in hydrocarbon solvents such as toluene, *n*-heptane and iso-octane.

The graphite used to prepare the pellets is preferably ground graphite prepared by ball milling graphite in vacuum or a gas e.g. air.

The grinding of the graphite gives small particles with a plate like graphite structure. Most of the surface area is contributed by the basal planes of the plates, but there is also a significant contribution made by the edges. For air ground graphite the ratio of basal plane surface area to edge surface area in a typical instance is about 4.5:1.

As previously described the graphites thus produced have the capability of absorbing normal hydrocarbons on the basal plane surface area and polar compounds, e.g. aromatics, sulphur and nitrogen compounds on the edge surface area. By adjustment of the feedstock and process conditions as described hereunder, the selectivity for either type of compound can be varied.

Thus according to another aspect of the present invention a process for the separation of normal hydrocarbons and/or polar compounds from their mixtures with other hydrocarbons comprises contacting the mixture with graphite pellets as hereinbefore defined to selectively adsorb said normal hydrocarbons and/or polar compounds.

The graphites before compounding with the binder preferably have a surface area of at least 50 square metres per gram and more preferably have a surface area of at least 300 square metres per gram.

The feed mixture for the process may be a petroleum distillate or residue boiling above 30°C, particularly a fraction in the waxy distillate boiling range i.e. 300 to 700°C or a waxy raffinate or a dewaxed raffinate. The feed may be a straight run fraction or a waxy raffinate obtained after a selective solvent treatment with e.g. furfural to remove aromatics. The feed may also be a solvent treated dewaxed lubricating oil fraction or hydrocracked gas oil the treatment in this case being a finishing treatment to improve colour and oxidation stability.

The process can also be used for removing

polynuclear aromatic compounds e.g. 3,4, benzo pyrene from lubricating oils and waxy distillates.

The absorption and desorption stages of the process of the invention are preferably carried out in the presence of liquids in which the adsorbed and subsequently desorbed components are soluble. These liquids may be the same or different. Thus, the liquid may comprise a single paraffin hydrocarbon, such as *n*-heptane or iso-octane, or it may comprise a mixture of hydrocarbons including refinery streams such as Primary Flash Distillate or an aromatic or alcoholic solvent may be used. The solvent used for dewaxing is preferably a polar solvent since such solvent promotes the absorption of non-polar compounds, such as waxes, including long chain *n*-paraffins. For the removal of polar compounds, the preferred solvent is a *n*-paraffin.

The adsorption stage of the process of the invention may be performed at a temperature of from -50°C to 200°C. If a mixture of paraffins, aromatics or alcohols is used its boiling range should be within this range. Hydrocarbons whose atmospheric boiling point is outside this range may be used at sufficient pressure to achieve a boiling point within the range quoted, provided that the desorption temperature is not above the critical temperature. Thus, for example, liquified propane and butane (L.P.G.) may be used under certain conditions.

For processing waxy raffinates and distillates a solvent is preferred. For a mobile liquid feedstock such as gas oil or kerosene no solvent is required.

The loading of the graphite with the absorbed components will depend on the nature of the feed, but should desirably be as low as possible. The loading expressed as graphite: feed ratio by wt is preferably less than 1:2, and more preferably less than 1:1 wt. The ratio of absorbed components to graphite may, however, be as low as 1:100. When refining waxy raffinates or distillates with dewaxing as the prime objective the overall graphite:feed ratios usually be in the range 1:1 to 10:1. If a multistage batch treatment is being used the individual stage graphite:feed ratios may be in the range 0.5:1 to 4:1.

When applying a polishing treatment to a dewaxed raffinate with the object of removing aromatics, heterocyclic, sulphur compounds and coloured materials, the overall graphite:feed ratios may be in the range 0.5:1 to 4:1.

The feed solvent/feed ratios can vary from 0:1 and 50:1 by wt. Suitable contact times between the graphite and the feed may be from 1 minute to 24 hours. The adsorption of *n*-paraffins is promoted by low temperatures within the stated range, and the preferential adsorption of aromatics by higher temperatures. Thus, the temperature should not be above 100°C and preferably from 0 to 50°C

if it is desired to adsorb paraffins. The temperature may be above 30°C, and preferably from 50 to 200°C where aromatics are to be adsorbed.

- 5 The adsorbed hydrocarbons may be recovered from the graphite by contacting it with a liquid which may be the same as that of the adsorption stage, or a chemically identical or different liquid may be used. The use of the same solvent is preferred.

- 10 The temperature may be in the range from room temperature up to 1000°C and pressure may be applied to keep the material treated in the liquid phase.

- 15 Typically the temperature of desorption is in the range of 100–400°C.

Alternatively, certain feedstocks can be treated over the graphite alumina adsorbent in the gas phase.

- 20 The pressure at which desorption is carried out should be such as to maintain the eluting material in the liquid state and will accordingly be within the range 10 to 3000 psig. It will of course be determined by the vapour pressure of the eluting material at the desorption temperature. The contact time will be within the range 1 to 120 minutes. The solvent desorbate ratio is preferably from 1:1 to 100:1.

- 30 The method is desirably carried out in a cyclic type of operation, for example, by percolating the feed mixture together with liquid through a bed of graphite pellets, removing non-adsorbed feed material and liquid from the bed, stripping the liquid from the non-

- 70 viscosity at 38°C=220 centistokes viscosity index=67
60°C=64.34 " sulphur=3.18% wt
77°C=31.57 "
99°C=15.09 "

was mixed with the pelleted graphite and *iso*-octane under the following conditions:—

- 75 Loading by wt 5:1 (pellets:distillate)
Solvent *iso*-octane at 20 ml per g feedstock
Temperature ambient
Contact time 24 Hr.

- 80 The graphite pellets were prepared by mixing 75 gms of graphite obtained from Solid Lubricants Limited prepared by grinding in air in a cascade ball mill to a surface area of 375 m²/gm (B.E.T.) with 25 gms of "Baymal" (Registered Trade Mark) alumina and then milling the dry solids for 10 minutes. The mixture was then worked into a thick paste by adding water and extruded through a 3.175 × 10⁻³M die. The extrudate was dried in air, broken up into pellets of size 1/8" diameter and sintered in nitrogen for 24 hours at 400°C to yield pellets of size 1/8" diameter. The treated distillate (obtained in 55% wt yield) was separated from the pellets by filtration and removal of solvent and had the following properties:—

adsorbed feed material, desorbing the adsorbed material from the graphite with the liquid, removing the desorbed material and liquid from the bed, stripping liquid from the desorbed material, and re-contacting the graphite with the feed mixture. In such a fixed bed type of operation reaction conditions, in particular liquid flow rate, should be chosen so that the pressure drop across the bed is not excessive.

45 In the case of preparation of lubricating oil base-stocks, the feedstock may be treated by any number of adsorption/desorption cycles to give a desired pour-point and viscosity index. The pour point of the treated material will decrease as the extent of removal of adsorbed materials increases, but the yield will also decrease. Waxy raffinate fractions treated by the process of the invention have in general higher viscosity indexes, lower cloud and pour points and lower sulphur contents than fractions obtained by conventionally treating similar feedstocks. They also have better response to oxidation inhibitors. In addition to the oil products obtained, the adsorbed and subsequently desorbed material i.e. normal paraffins and/or aromatics may be of use, particularly if it is waxy paraffinic or aromatic hydrocarbon material.

65 The invention is illustrated by the following examples.

Example 1.

A Kuwait waxy distillate having a pour point of 38°C

Viscosity at 38°C 164.52 c St (220)
60°C 52.06 (64.34)
99°C 13.42 (15.09)
Viscosity index 80 (67)
Pour point (micro) +4°C (+38°C) 100

Figures in brackets refer to the original distillate.

Example 2.

A finished Kuwait/I meg lubricating oil having a viscosity of 110 centistokes at 100°F and a viscosity index of 95 determined in accordance with ASTM D 2270 was percolated through a bed of 14–100 BSS graphite alumina crushed extrudate under the following conditions:— 110

Solvent
Temperature
Space velocity
wt of adsorbent

iso-octane at 3 ml per g feedstock
ambient
0.365 vol/vol/hour contact time 2.74 hours
977 g length of bed 45 cms.

- 5 The graphite alumina adsorbent was prepared by mixing 3 parts by weight of graphite obtained from Solid Lubricants Limited and prepared by grinding in air in a cascade ball mill to a surface area of 375 m²/gm (BET) with 1 part of "Baymal" (Registered Trade Mark) alumina and then ball milling the dry solids for 10 minutes. The mixture was then worked into a thick paste and extruded through a 3.175 × 10⁻³M die. The extrudate was dried in air, sintered in nitrogen at 400°C for 24 h and crushed and sieved to yield 14—100 mesh BSS adsorbent.
- 10 The treated oil was collected in 9 fractions having the properties shown in Table 1. The results show that treatment with the graphite pellets improves the colour stability of the lubricating oil and removes aromatics, sulphur and nitrogen compounds.
- 15 Overall Yield of unadsorbed oil 97%
Overall graphite:feed oil ratio 0.082:1

TABLE 1

Fraction	Yield g	Micro Pour Point °F.	ASTM Colour	Sulphur Content % wt	Total Nitrogen ppm	Aromatic Carbon CA %
1	405.6	5	<0.5	0.67	9	2.6
2	1029.0	10	<1.0	0.97	31	3.5
3	1016.5	10	1.5	1.03	66	3.4
4	979.4		<1.5	1.04	85	3.8
5	1014.0		1.5	1.03	100	4.2
6	624.0		1.5	1.04	105	3.8
7	1277.0		<2.0	1.04	110	3.6
8	944.0		<2.0	1.06	110	3.7
9	1343.0		2.0	1.06	115	3.6
Feed	—	10	2.5	1.06	125	3.6

After passing the oil, the column was washed with iso-octane at 250°C and 274 g of waxes and aromatics recovered. After the desorption the feedstock was percolated again and 2 fractions collected comprising a total of 1855 g as shown in Table 2.

TABLE 2

Second Run

Fraction No.	Cumulative wt g	Oil to Graphite Ratio	ASTM Colour	S %	N ppm	CA
1	545	0.6:1	<1.0	—	24	—
2	1855	1.9:.		—	66	—

Example 3.
Extraction of Polynuclear Compounds by
Graphite/Alumina.

The pellets were prepared exactly as in

Example 2 but alumina manufactured by Laporte having a surface area of 2 m²/gm was used in place of Baymal (Registered Trade Mark) Alumina. The pellets were the same size as in Example 2 viz 4—100 mesh B.S.S.

Oil	Total UV Absorbance 280—400 mu +	3,4-Benzopyrene Ug/kg x
(a) A middle East waxy distillate The procedure of Example 2 was repeated but, 5 parts by weight of oil treated with 1 part of graphite/alumina at 50°C. with solvent	32.0 9.1	750 30
(b) Feed oil As in (a) above, 5 parts of oil treated with 1 part of graphite/alumina at 50°C. without solvent As above, 1:1 treatment with graphite/alumina at 20°C. in isooctane	9.4 6.2 0.6	150 20 <10
(c) SAE 10 lubricating oil prepared by hydrogenation of a Kuwait vacuum distillate. As in (a) and (b) above 5 parts of oil treated with 1 part of graphite/alumina at 50°C. no solvent	2.7 0.1	100 <10

x determined by liquid chromatography and UV spectroscopy.

+ determined by FDA 121.2589 (c).

The oil used in Example 3 (a) had the following inspection data:

Kinematic viscosity at	100°F.	20.5 centistokes
	140°F.	9.6 "
	210°F.	3.86 "

Specific Gravity 60/60 0.901

The oil used in Example 3 (b) gave the following Vacuum

Engler distillation data.

Initial listing point	343
10% distilled	383
50% "	414
90% "	450
Final listing point	472
Kinematic viscosity at	100°F. 20.5 centistokes
	140°F. 9.6 "
	210°F. 3.86 "

Specific Gravity 60/60 0.8805.

Example 4.

Graphite Treatment of a Hydrocracked Gas Oil.

- 5 The pellets were prepared exactly as described in Example 3 and the hydrocracked gas oil, boiling range 225°C—370°C, was percolated through graphite/alumina pellets without solvent at room temperature, the products

being collected at oil to graphite ratios of 10 20:1 and 35:1.

The percolated oils have been found to be much lighter in colour and had a significantly greater stability to light and heat compared with the feedstock as shown in the table 15 below.

Test	Feedstock	Percolated Oils	
		Oil to Graphite Ratio 20:1	Oil to Graphite Ratio 35:1
Colour, ASTM	<3.5	<0.5	<0.5
Exposure to sunlight, 1 day on window sill	light brown deposit	no deposit, oil clear	no deposit, oil clear
*DEF 2060 test, Method 16 (heating at 210°F. for 16 hours)			
Total sediment, mg/100m	0.23	0.1	0.06

* Ministry of Defence test.

These results show that 'polishing' of gas oils by percolation through graphite/alumina absorbents increases substantially their stabilities to light and heat.

The graphite had a surface area of 380 m²/gm and the alumina 300 m²/gm.

The minimum of water, about 30 grams, was added gradually with continuous mixing to give a firm smooth paste.

The paste was extruded through $\frac{1}{8}$ inch diameter die. The extrudate was allowed to dry slowly overnight and then sintered in nitrogen at 400°C.

The sintered material has the physical properties shown in Table I below:

TABLE I

Graphite/Alumina GB 300 6 — 25 BSS mesh

BET Surface Area,	m ² /g	355
Bulk Density	Maximum	0.61 gms/cc
		0.52 mgs/cc

25 Separation of a Waxy Raffinate having a viscosity of 110 centistokes at 100°F and a viscosity index of 95 determined in accordance with ASTM D 2270 over a column of Graphite alumina absorbent. A column 89 centimetres long and 5.7 centimetres square cross section was filled with 300 grams of 30 6—25 BSS mesh crushed graphite/alumina extrudate.

A solution of 56.25 grams of the waxy

Raffinate of Kuwait origin in 500 millilitres of isooctane was pumped through the column at a flow rate of 200 mls per hour and a residence time of 2 hours. The removal of fractions of the unadsorbed oil was effected by pumping isooctane through the Column. Equal volumes of solution issuing from the Column gave the following yields and pour points when the oil was isolated. The temperature of the elution was 22°C.

TABLE II

Absorbent Graphite (75%) Pechiney GB 300 alumina (25%) 6—25 BSS mesh.

— weight	300 gms
Eluent	isooctane
Flow rate	200 mls/hr
Residence Time in Column	2 hours
Charge Oil Kuwait Waxy Raffinate	
Charge Weight	56.25 grams
Pour Point of Feed	100°F.
Wax content of feed	19.9% wt
Products.	
Eluted with isooctane	
Fraction I weight percent	6.2
Pour point °F.	—3 5
Fraction 2 Weight percent	23.5
Pour Point °F.	+5
Fraction 3 weight percent	17.2
Pour point °F.	+ 3 5
Fraction 4 weight percent	9.8
Pour point °F.	+ 40
Fraction 5 weight percent	5.3
Pour point °F.	+ 5 5
Fraction 6 weight percent	3.9
Pour point °F.	+ 50
Fraction 7 weight percent	4.6
Pour point °F.	60
Fraction eluted with hot Ethylene Dichloride 150°C. wt%	14.6
Pour point °F.	>100

WHAT WE CLAIM IS:—

1. Graphite-containing pellets comprising graphite with a binder comprising finely divided alumina (as herein defined) said graphite being a vacuum or gas ground graphite having a surface area of 50 to 2000 m²/gm (BET).
2. Graphite-containing pellets as claimed in claim 1 wherein the alumina has a surface area of 100 to 600 m²/gm.
3. Graphite-containing pellets as claimed in either of claims 1 or 2 wherein the pellets have a particle size in the range 4 to 200 mesh

BSS and contain from 5 to 50% by weight of alumina. 15

4. A process for the preparation of graphite-containing pellets which process comprises intimately mixing a vacuum or gas-ground graphite powder having a surface area of 50 to 2000 m²/gm with a finely divided alumina binder (as herein defined), working the mixture into a paste and then granulating or extruding through a die. 20

5. A process as claimed in claim 4 wherein, after extrusion, the extrudate is broken up and sintered in an inert atmosphere. 25

6. A process as claimed in either claim 4 or claim 5 wherein the surface area of the graphite before compounding is at least 50 m²/gm.
- 5 7. A process as claimed in any one of claims 4 to 6 wherein the alumina employed is a hydrated alumina.
8. A process for the separation of normal hydrocarbons and/or polar compounds from their mixtures with other hydrocarbons comprising contacting the mixture with graphite pellets as claimed in any one of claims 1 to 3 and controlling the process conditions in such a manner to selectively absorb the normal hydrocarbons and/or polar compounds.
- 10 9. A process as claimed in claim 8 wherein the feed is a petroleum fraction boiling in the range 300 to 700°C and the process is effected in adsorption and desorption stages.
- 15 10. A process as claimed in either claim 8 or 9 wherein the process is effected in the presence of a liquid in which the adsorbed and subsequently desorbed component are soluble.
- 20 11. A process as claimed in claim 10 for the removal of waxes wherein a polar solvent is employed.
- 25 12. A process as claimed in claim 10 for the removal of polar compounds wherein a n-paraffin solvent is employed.
- 30 13. A process as claimed in claim 8 for the removing aromatics, heterocyclics, sulphur compounds and coloured materials from a dewaxed raffinate wherein the overall graphite feed ratio by weight is in the range 0.5:1 to 4:1.
14. A process as claimed in claim 8 for improving the heat and colour stability of a hydrocracked gas oil or a lubricating oil which process comprises contacting the gas oil or lubricating oil with graphite pellets as claimed in any one of claims 1 to 3.
15. A process as claimed in claim 8 for removing polynuclear aromatic compounds from lubricating oils and waxy distillate with graphite pellets as claimed in any one of claims 1 to 3.
16. A process for the preparation of graphite-containing pellets substantially as hereinbefore described with reference to any one of the Examples.
17. A process for the separation of normal hydrocarbon and/or polar compounds substantially as hereinbefore described with reference to any one of the Examples.
18. Graphite pellets whenever prepared by a process as claimed in any one of claims 4 to 7 or 16.
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Details for CN 1338450 A**Title**

Process for refining toluene containing nitrogen impurities

Patent Assignee

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Inventor

DUAN Q; GU K; YANG M

Accession Number

2002-372856 [41] WPIX

Abstract

CN 1338450 A UPAB: 20060202

NOVELTY - A process for refining toluene containing nitrogen impurities features that said toluene is in contact with sulfonate-type cationic exchange resin layer at ordinary temp-80 deg.C and linear speed lower than 10 m/hr to remove said impurities.

ADVANTAGE - Advantages include high effect and low cost.

Patent Information

PATENT NO.	KIND	DATE	WEEK	LA	PG	MAIN IPC
CN—1338450	A	20020306	(200241)*	ZH		
CN—1142127	C	20040317	(200577)	ZH		

Priority Application Information

Application Number	Date
2000CN-000121552	20000811

Details of non-patent literature

(Full copies will be provided with the confirmation copy of this letter).

Title
Adsorption process for removal of nitrogen and sulphur

Source
NPRA Annual Meeting (San Antonio March 1999) (Adaptation) Petroleum Technology Quarterly V4 N.2 37-40,42,44 (Summer 1999). ISSN: 1362-363.

Author
Irvine R L; Varraveto D M

Corporate Source
Black & Veatch Pritchard Inc

Document Type
Conference

Language
English

Accession Number
1999:13774 ENCOMPLIT;ENCOMPLIT2

Abstract
Adsorption process for removal of nitrogen and sulphur. The Irvad process was developed by Black & Veatch Pritchard and Alcoa Industrial Chemicals to treat liquid hydrocarbon streams with $\leq 240^{\circ}\text{C}$ ebp, primarily FCC gasoline and coker naphtha, through countercurrent contact with a solid adsorbent, SAS, in a multi-stage fluidized adsorber. SAS is an alumina-based sorbent modified with inorganic promoters to maximize its sorption capacity for polar nitrogen and sulfur compounds. The adsorbent is regenerated continuously by high-temperature contact with a reactivating gas. With the second-generation adsorbent, SAS-2, > 92% sulfur and > 99.5% nitrogen removal from a full boiling range FCC gasoline was achieved. High liquid yields coupled with an octane gain give this technology an advantage for olefinic feedstock treating over conventional approaches. The process operates at lower pressure, with lower energy consumption, does not consume $\text{H}(\text{sub})_2$ or saturate olefins, and produces no hazardous waste. It can also be used to treat visbreaker naphtha, pyrolysis gasoline, H-Oil or LCfining naphtha, and CanMet naphtha. Other possible applications are pretreatment of $\text{C}(\text{sub})_3\text{-C}(\text{sub})_5$ olefin feeds and saturate streams like LPG, iso- $\text{C}(\text{sub})_4$ feed to alkylation, and $\text{C}(\text{sub})_5/\text{C}(\text{sub})_6$ feeds to isomerization. Pilot tests are being planned to treat natural gasoline or condensate to reduce their sulfur contents to < 10 ppm and nitrogen contents to negligible levels. Diagrams and graphs.

Title
THE COMPETITIVE ADSORPTION OF FUEL-TYPE COMPOUNDS ON ZEOLITE 13X

Source
192ND ACS NATL. MEET. (ANAHEIM 9/7-12/86) ACS DIV. FUEL CHEM. PREPR. V31 N.3 262-65 (1986).

Author
JEAN G; CHANTAL P; AHMED S; SAWATSKY H

Corporate Source
CAN. CENT. MINER. ENERGY TECHNOL. . CENT. MINER. ENERGY TECHNOL.

Language
English

Accession Number
86:8285 ENCOMPLIT;ENCOMPLIT2

Abstract
The competitive adsorption of fuel-type compounds on zeolite 13X. As part of a study on attempted selective adsorption of organonitrogen compounds from petroleum fractions and synthetic fuel fractions onto a 13X zeolite as a possible alternative to hydrotreating, degrees of competition between model organonitrogen compounds and other model organic compounds (mainly olefins and oxygenates) in adsorption from dilute toluene solutions were determined experimentally in a continuous-flow fixed-bed adsorption column, to test the previous proposal [ACS Div. Fuel Chemical Prepr. 30 #4:474-80 (1985)] that unexpectedly low adsorption of nitrogen compounds from a naphtha was due to competitive adsorption of non-nitrogen compounds. Most non-nitrogen compounds actually competed very little

with nitrogen compounds, and olefins competed only at very high olefin concentrations. The capacities of the zeolite for several weakly basic nitrogen compounds (e.g., phenethylpiperidine and collidine) were low, and would decrease in multicomponent solutions due to site competition. An absorption process using 13X for the removal of heteroatom compounds from complex fuel fractions would thus be inefficient. Tables.

Title SELECTIVE REMOVAL OF NITROGENOUS COMPOUNDS (FROM PETROLEUM FRACTIONS BY) USING ZEOLITES

Source 190TH ACS NATL. MEET. (CHIC. 9/8-13/85) ACS DIV. FUEL CHEM. PREPR. V30 N.4 474-80 (1985).

Author JEAN G; BONVIE E; SAWATZKY H

Corporate Source CAN. CENT. MIN. ENERGY TECHNOL.

Language English

Accession Number 85:6285 ENCOMPLIT;ENCOMPLIT2

Abstract

Selective Removal of Nitrogenous Compounds [from Petroleum Fractions by] Using Zeolites was investigated as a potential alternative to expensive hydrotreating. In experiments with a model solution containing 18 nitrogen compounds (NC) in toluene and having a total nitrogen content of 518 ppm, a 13 X sodium zeolite showed a total nitrogen sorption capacity of 100 mg/g zeolite, but the degree of sorption of individual NC's strongly decreased with increasing molecular size, from maximum values for small basic NC's to very low values for three- and four-ring neutral NC's. In tests on a coker naphtha (24.6 wt % paraffins, 61.8% olefins, 0% naphthenes, 13.6% aromatics, 0.002% nitrogen) and a hydroprocessed naphtha (55, 15, 19, 10, 0.005%), the nitrogen sorption capacities of the 13 X zeolite, 4.6 and 14.2 mg/g, respectively, were much lower than expected from a model compound study. This result was attributed to competitive adsorption of NC's and other components (olefins, aromatics) of the naphthas. The relative sorption selectivities of the zeolite for various NC's was somewhat modified by cation exchange. Tables, graphs, and 14 references.

Title ELUCIDATION OF THE IRON CHLORIDE/CLAY SYSTEM FOR REMOVAL OF NITROGEN-CONTAINING COMPOUNDS FROM PETROLEUM AND SHALE-OIL DISTILLATES

Source FUEL V63 N.10 1472-74 (OCT. 1984). ISSN: 0016-2361.

Author RAYNER-CANHAM G W; DICKERHOOF D W

Corporate Source MEM. UNIV. NEWFOUNDLAND ; COLO. SCH. MINES

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Abstract

Elucidation of the Iron Chloride/Clay System for Removal of Nitrogen-Containing Compounds from Petroleum and Shale-Oil Distillates. Anhydrous ferric chloride, a strong Lewis acid, was adsorbed very rapidly from a saturated toluene solution onto attapulgus clay, which was then dried to a powder. Pyrazole, quinoline, carbazole, and N-ethylcarbazole were removed very rapidly from toluene or pentane solutions (models for petroleum and shale-oil distillates) by complexation with the adsorbed ferric chloride, more efficiently than by hydrated ferric chloride adsorbed onto attapulgus clay from methanol or onto silica. In toluene, quinoline and pyrazole complexed the adsorbed ferric chloride into solution; but in pentane, these complexes were retained on the clay. Solubilization of ferric chloride could thus be a problem in the treatment of aromatic-rich distillates. Table and 21 references.